

INTERACTION BETWEEN COAL AND METHANE
DURING ENTRAINED-FLOW FLASH PYROLYSIS
IN RELATION TO ENHANCEMENT IN ETHYLENE YIELD

Muthu S. Sundaram* and Meyer Steinberg
Process Sciences Division
Brookhaven National Laboratory
Upton, NY 11973

ABSTRACT

The flash pyrolysis of coal in a methane atmosphere leads to a significant improvement in total ethylene production by comparison with pyrolysis in an inert helium atmosphere. A study was undertaken to determine the fractional contribution of coal and methane feed toward formation of ethylene. The analytical method entails determination of ^{13}C distribution in coal, methane feed, and product ethylene. The ^{13}C distribution in alkyl side chains (or polymethylene moieties) of coal, which are considered to be likely precursors for ethylene, was found to be higher than in the remaining carbon skeleton. The data available show an interaction between methane and coal during entrained-flow flash pyrolysis of coal with methane with respect to the increase in ethylene yield. At 1000°C and 50 psi methane, with a methane to coal ratio of 1.2, ethylene concentration in the product stream is 1.3% by volume. Of this, 41.8% is produced from coal and the remaining 58.2% is from methane feed. This corresponds to a carbon conversion of 1.9% from methane and 1.6% from coal.

KEYWORDS: Coal; pyrolysis; gasification; methane; ethylene; isotope ratio; carbon.

INTRODUCTION

Traditionally, flash pyrolysis of coals for the production of fuels and chemicals has been carried out in a reactive hydrogen atmosphere and non-reactive helium, nitrogen, and argon atmospheres. The fundamental aspects of primary devolatilization of coal and secondary cracking of volatiles in the above gas media have been investigated extensively under various reaction conditions.

Over the past few years, Brookhaven National Laboratory has investigated the possibility of using methane (or natural gas) as an entraining gas in coal pyrolysis studies. Pyrolysis of coal in a methane atmosphere resulted in enhanced ethylene and BTX yields over those obtained by the flash pyrolysis of coal in an inert helium atmosphere under the same conditions of temperature and pressure.^(1,2)

The objective of the present study was to understand the role of methane in enhancing ethylene production. Originally, experiments were

*To whom correspondence should be addressed.

planned tagging the methane gas with a known amount of $^{13}\text{CH}_4$. However, this approach was economically impractical, since each experiment would use several hundred litres of expensive CH_4 - $^{13}\text{CH}_4$ gas mixture. This prompted us to look for other alternatives, and a successful attempt was made taking advantage of the small difference in the natural abundance of ^{13}C in coal and methane.

The focus was on product ethylene rather than on producing a complete ^{13}C material balance. Accordingly, this paper deals with the question: How much of the ethylene in the product stream is produced from coal and how much from methane feed?

EXPERIMENTAL

The flash pyrolysis experiments were carried out in an externally heated 1-in.-diameter-by-8-ft-long downflow entrained tubular reactor. Preheated helium and unlabeled methane gases were fed into the reactor to a pressure of 50 psi. A New Mexico subbituminous coal, with analysis shown in Table 1, was used in the study. The coal, premixed with 10% by weight of Cab-O-Sil (a fumed silica powder) to prevent agglomeration, was dried in a vacuum oven overnight. The particle size of the coal was 150 μm or less, and coal from the same batch was used in pyrolysis experiments reported here. The high temperature gas feed is mixed at the top of the reactor preheating the gases at optimum conditions of temperature, coal-feed rate and gas-feed rate chosen from previous studies so that a high concentration of ethylene was obtained in the product stream.

Routine gas analyses were performed in an on-line GC. In addition, grab samples of product gas mixture were collected in steel gas cylinders, and the components in the gas mixture were separated from each other in a conventional GC/MS system using a 6-ft Carbosieve S column. The compositions of normal ethylene (C_2H_4) and heavy ethylene ($^{13}\text{CCH}_4$) in the mixture were determined by selectively monitoring ions due to masses 28 and 29. A typical example of ion profiles for masses 28, 29, 30, and 44 is shown in Figure 1. The nitrogen peak is an impurity arising from the use of a gas-tight syringe for transfer of gas samples from steel cylinders to the injection port of the GC/MS. From the integrated peak area, the $^{13}\text{C}/^{12}\text{C}$ ratio for product ethylene is readily calculated.

RESULTS AND DISCUSSION

The natural abundance of ^{13}C isotope is 1.1%. During the process of photosynthesis, there is a discrimination against $^{13}\text{CO}_2$ in the rate of assimilation when compared to that of CO_2 .⁽³⁾ As a result of this isotope fractionation, wood, crude oil, and coal are enriched in ^{12}C by about 20 to 30 ‰. The isotopic constitution of carbon in some samples of coal, wood, and methane gas frequently used in our laboratory is shown in Table 2. Methane is lighter than either coal or biomass. An appreciable difference in ^{13}C enrichment between coal or biomass and methane is seen

Table 1

Analysis of New Mexico Coal (wt %)

Rank: Subbituminous

Moisture (as received): 7.8

Proximate Analysis (dry):

Volatile Matter : 34.9
 Fixed Carbon : 42.4
 Ash : 22.4

Ultimate Analysis (dry):

Carbon : 55.9
 Hydrogen : 4.3
 Nitrogen : 1.1
 Sulfur : 1.0
 Oxygen : 14.9
 (by diff.)

Table 2

Isotopic Constitution of Carbon in Selected Materials

Feedstock	$\delta(^{13}\text{C}), \text{‰}^*$	$^{13}\text{C}/^{12}\text{C}$	$^{12}\text{C}/^{13}\text{C}$
Douglas Fir Wood	-23.3	0.01098	91.11
Sugar Pine Wood	-24.1	0.01097	91.19
Illinois No. 6 Bituminous Coal	-25.7	0.01095	91.34
New Mexico Subbituminous Coal	-27.0	0.01093	91.46
Methane	-41.4	0.01077	92.85

*Analyses reported in parts per mil (‰) and computed as follows:

$$\delta^{13}\text{C}_{\text{sample}} = \frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}} - 1 \times 1000$$

where, $^{13}\text{C}/^{12}\text{C}_{\text{standard}}$ is CO_2 from *Belemnitella americana*, Cretaceous, Pee Dee formation, South Carolina, USA, Chicago (PDB) standard.

and $^{13}\text{C}/^{12}\text{C}_{\text{standard}} = 0.0112372$

in Table 2. A small enrichment in ^{13}C is observed in a higher-rank Illinois No. 6 bituminous coal when compared with a lower-rank New Mexico sub-bituminous coal. Monin reported a progressive increase in $\delta(^{13}\text{C})$ found in a series of coals from the Mahakam delta, Indonesia.⁽⁴⁾ The $\delta(^{13}\text{C})$ value increased from $-29.5\text{ }^{\circ}/_{\text{oo}}$ at the peat-lignite level to $-27.6\text{ }^{\circ}/_{\text{oo}}$ at the bituminous A level.

A vast literature exists on the partial oxidation and thermal cracking of methane under various conditions. An excellent review of articles on this subject is available in Reference 6. Methane, however, did not undergo homogeneous decomposition in the BNL reactor. The Cab-O-Sil additive, spent char, and reactor walls made of Inconel 617 alloy were also found not to promote the cracking of methane to ethylene in the absence of coal.

The New Mexico subbituminous coal was pyrolyzed in a methane atmosphere at 1000°C . The same coal was pyrolyzed in a helium atmosphere for comparison. The gas feed rates, in terms of lb-mole per hour, were kept identical in both atmospheres. The reaction conditions and the product yields are shown in Table 3. The yields are customarily reported as percent conversion of carbon contained in the feed coal to product.

The $^{13}\text{C}/^{12}\text{C}$ ratios of product ethylene under various experimental conditions obtained from GC/MS analyses with an error of $\pm 2\%$, are shown in Table 4. The following points are noteworthy: (1) In inert helium atmosphere, the $^{13}\text{C}/^{12}\text{C}$ ratio for ethylene is higher than for the original coal. If ^{13}C atoms were uniformly distributed throughout the coal "structure," one would not expect this fractionation effect. To explain this nonhomogeneity in ^{13}C distribution in the coal matrix, it is suggested that the ^{13}C distribution in alkyl side chains (or polymethylene moieties) of coal, which are considered to be likely precursors for ethylene,⁽⁵⁾ is higher than in the remaining carbon skeleton. This suggests that the origin of these alkyl side chains is different from the rest of the coal. This might be due to a different kind of plant material, a diagenesis organism, or something else. (2) In helium atmosphere, the concentration of ethylene in the product stream decreases from 0.65% at 900°C to 0.35% at 1000°C . However, the concentration in the product stream or the pyrolysis temperature does not affect the $^{13}\text{C}/^{12}\text{C}$ ratio for ethylene. (3) Ethylene concentration increases substantially when the coal is pyrolyzed in methane. (4) The $^{13}\text{C}/^{12}\text{C}$ ratio for ethylene from methanolysis experiments lies between that from a helium run and the $^{13}\text{C}/^{12}\text{C}$ ratio for methane feed. This indicates that a part of ethylene in the product stream comes from coal and the remaining from the methane feed.

On the basis of ^{13}C material balance with respect to product ethylene, the actual fractional contributions of coal and methane feed in the formation of ethylene can be determined. For this analysis, the following assumptions are made:

Table 3

Product Yield Data

Reactor Temperature, °C	900	1000	1000
Entraining Gas	He	He	CH ₄
Gas Pressure, psi	50	50	50
Coal Feed Rate (lb/hr)	1.81	1.81	3.84
Gas Feed Rate (lb/hr)	1.04	1.04	4.74
Gas Feed Rate (lb-mole/hr)	0.26	0.26	0.29
Particle Residence Time (sec)	1.5	1.5	1.5

Product Yields*

CH ₄	5.4	6.7	ND
C ₂ H ₄	3.3	1.7	3.2 ⁺
C ₂ H ₆	0.3	0	0.5
BTX	3.5	3.3	5.9
CO	4.6	7.2	5.3
CO ₂	1.8	2.1	1.8

* All yields based on the carbon contained in coal.

⁺ Corrected to 1.6% after subtracting the contribution from the methane feed.

Note: The difference in the coal flow rates was not great enough to cause a significant change in ethylene yields.

Table 4

Isotopic Constitution of Carbon in Product Ethylene

Entraining Gas	Temperature °C	Ethylene Concentration (mole %)	¹³ C/ ¹² C*	¹³ δ ⁺
Helium	900	0.65	0.01295	0.01278
"	1000	0.35	0.01295	0.01278
Methane	1000	1.3	0.01167	0.01154
"	-	-	0.01077	0.01065

• Average of three analyses from samples collected under specified conditions.

⁺ Not to be confused with δ(¹³C), ‰.

This is concentration of ¹³C atoms in the total of (¹²C + ¹³C).

- (1) At given temperature and pressure conditions, the devolatilization characteristics of coal are the same in both helium and methane atmospheres.
- (2) The $^{13}\text{C}/^{12}\text{C}$ ratio is not affected by the coal feed rate.
- (3) The kinetic isotope effect involving ^{13}C and ^{12}C atoms is negligibly small.

Setting up a material balance for ^{13}C in ethylene, we have

$$W_m f_m {}^{13}\delta_m + W_c f_c {}^{13}\delta_c = \Delta_e {}^{13}\delta_e \quad (1)$$

W_m = Amount of carbon in methane feed.
 W_c = Amount of carbon in coal feed.
 f_m = Fraction of carbon in methane converted to ethylene.
 f_c = Fraction of carbon in coal converted to ethylene.
 Δ_e = Total carbon in product ethylene.
 ${}^{13}\delta_m$ = Concentration of ^{13}C in methane feed.
 ${}^{13}\delta_c$ = Average concentration of ^{13}C in coal.
 and ${}^{13}\delta_e$ = Concentration of ^{13}C in product ethylene in methane atmosphere.

The effective concentration of ^{13}C in coal involved in the formation of ethylene, as measured in an inert helium atmosphere, can be related to the average concentration of ^{13}C in whole coal by the following expression:

$${}^{13}\delta_c = \alpha {}^{13}\delta_H, \quad (2)$$

where

${}^{13}\delta_H$ = effective concentration of ^{13}C in coal involved in the formation of ethylene
 α = inhomogeneity factor.

Substituting for ${}^{13}\delta_c$ and dividing both sides of Eq. (1) by Δ_e we have

$$X_m {}^{13}\delta_m + X_c {}^{13}\delta_H = {}^{13}\delta_e, \quad (3)$$

where

$$X_m = W_m f_m / \Delta_e \quad (4)$$

= ratio of ethylene produced from methane feed to total ethylene produced.

$$X_c = \alpha W_c f_c / \Delta_e \quad (5)$$

= ratio of ethylene produced from coal to total ethylene produced.

From the definitions for X_m and X_c in Eqs. (4) and (5), it follows that

$$X_m + X_c = 1.0 \quad (6)$$

$^{13}\delta_m$, $^{13}\delta_H$, and $^{13}\delta_e$ are experimentally determined and α can be calculated from $^{13}\delta_H$ and $^{13}\delta_c$. Now, Eqs. (3) and (6) can be solved to obtain the values for X_m and X_c .

Using the data shown in Table 4, X_m and X_c are calculated to be 0.5822 and 0.4178, respectively, which, since the kinetic isotope effect between ^{13}C and ^{12}C is negligibly small, means that 58.22% of the ethylene in the product stream is produced from methane feed and the remaining 41.7 originated in coal under the conditions employed. This corresponds to a carbon conversion of 1.92% from methane and 1.58% from coal. The effect of interaction between coal and methane in enhancing the total yield of ethylene is, thus, clearly indicated. Conversion of methane to ethylene in the presence of coal, as observed by the authors is somewhat higher than the 0.9 - 1.0% conversion reported by Calkins from pyrolysis of methane alone at 850°C for 0.5 sec in a fluidized-bed reactor after having pyrolyzed Alcoa Texas lignite in it.⁽⁷⁾ The higher carbon conversion in BNL experiments is attributed to the higher temperature (850°C vs. 1000°C) and increased residence time (0.5 sec vs. 1.5 sec). Furthermore, the mineral matter or char from the New Mexico sub-bituminous coal used in our study could have been catalytically more active than the lignite used by Calkins et al.

Though this study establishes that interaction between coal and methane effects total ethylene production, it is still not clear whether the yield enhancement is due to catalytic cracking of methane on the coal surface or due to chemical reaction of methane with "reactive" (free radical) species generated from coal. It is our speculation that the mechanism is associated with reaction of methane gas with high-temperature-coal-pyrolysis tar. Reaction studies using representative model compounds can give greater insight into the actual mechanism. Further investigation with a complete ^{13}C material balance between reactants and all products under different coal and methane feed rates is warranted.

CONCLUSION

Pyrolysis of coal in methane atmosphere leads to a significant improvement in total ethylene production when compared to pyrolysis in an inert helium atmosphere. This is due to an interaction between methane and coal during entrained-flow flash pyrolysis. At 1000°C and 50 psi pressure of methane, and a methane-to-coal ratio of 1.2, 1.9% carbon from the methane feed, and 1.6% carbon from the coal feed were converted to produce ethylene resulting in a concentration of 1.3 vol. % in the effluent gas stream.

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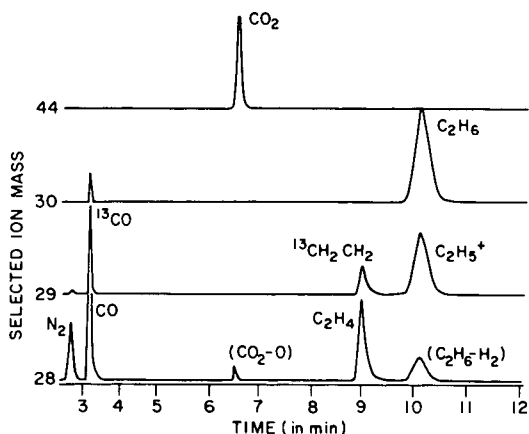


Figure 1. Selected Ion Chromatogram of Gaseous Products from Pyrolysis of New Mexico Sub-bituminous Coal in 50 psi Methane at 1000°C.